VIBRONIC EMISSION SPECTROSCOPY OF JET-COOLED CHLORO-SUBSTITUTED BENZYL-TYPE RADICALS PRODUCED BY CORONA DISCHARGE

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Whereas benzyl radical, a prototype of aromatic free radicals, had attracted much attention from spectroscopists for the subject of large molecular radicals, chloro-substituted benzyl–type radicals have been little studied, presumably due to the difficulties associated with production in corona discharge from precursors. The weak C-Cl bond can be easily dissociated in high voltage corona discharge, [a] leading to the cleavage of benzene ring. During past years, we have concentrated on the spectroscopic observation of chloro-substituted methylbenzyl radicals in a technique of corona excited supersonic expansion using a pinhole-type glass nozzle which has been well developed in this lab. From the experiments, we could succeed the observation of vibronic emission spectra of chloro-substituted methylbenzyl radicals from 3- and 4-chloro-o-xylenes. From the analysis of the spectra observed, we can identify the radical species produced in corona discharge and determine the electronic energies of the $D_1 \rightarrow D_0$ transition. The variation of the electronic transition energies with the positions and types of substituents have been clearly explained by means of the additivity rule [b] and shape of the unoccupied lowest molecular orbitals (LUMO) which corresponds to the upper state of the electronic transition. In this presentation, the observation scheme of the chloro-substituted benzyl-type radicals and analysis of the spectra for the identification of the radical species generated will be discussed, together with the introduction of the method for the explanation of substituent effect [c] on the electronic transition energy of the benzyl-type radicals.

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[a] S. Y. Chae, M. Lim, and S. K. Lee, *Chem. Phys. Lett.* **664**, 242-245 (2016).

[b] Y. W. Yoon, S. Y. Chae, and S. K. Lee, *Chem. Phys. Lett.* **644**, 167-170 (2016).

[c] C. Branciard-Larcher, E. Migirdicyan, and J. Baudet *Chem. Phys.* **2**, 95-106 (1973).